California Environmental Protection Agency

Air Resources Board

Engineering and Laboratory Branch
Monitoring and Laboratory Division

MLD SOP ES05

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF EXEMPT COMPOUNDS IN AEROSOL CONSUMER PRODUCT PROPELLANT BY GAS CHROMATOGRAPHY

March 10, 1998, Revision 2

1 INTRODUCTION

This document describes a procedure for the analysis of aerosol consumer product propellants containing "exempt" compounds as identified under Title 17, California Code of Regulations, Division 3, Chapter 1, Subchapter 8.5, Articles 1 and 2, Sections 94500-94517. Under the regulations, the following gaseous compounds are exempt from the definition of "Volatile Organic Compounds (VOC): carbon monoxide, carbon dioxide, methane, ethane, 1,1-diflouroethane (R-152a), 1,1,1-triflouroethane (R-143a), triflouromethane (R-23), and 1,1,1,2-tetraflouroethane (R-134a). At this time, it is expected that only R-152a, R-134a, and CO_2 will be used in products. For more information see ARB Method 310, U.S EPA Method 18, U.S EPA Method 8240, ASTM D 859-88 and NIOSH 1400.

2 SUMMARY OF METHOD

This procedure measures exempt propellant compounds using a gas chromatography/TCD technique. The procedure is presented in two parts: a propellant collection procedure and the propellant analysis by gas chromatography. The aerosol product container is pierced and the propellant is bled into an evacuated manifold. After the manifold reaches atmospheric pressure, approximately 1 liter of the propellant is collected in an, evacuated tedlar bag. In addition, the propellant is collected into an evacuated 250 ml glass dilution bulb that has been weighed to the nearest 0.1 mg. After filling, the dilution bulb is re-weighed to determine the density of the propellant. The tedlar bag with the propellant aaquot is taken to the laboratory for analysis. An aliquot of the propellant is injected into a gas chromatograph (GC) equipped with a Carboxen 1006 PLOT capillary column and the propellant separated into its components. Concentrations greater than 0.1% by weight in the propellant are reported.

3 INTERFERENCES/LIMITATIONS

3.1 In this procedure, it is assumed that most aerosol propellants will be a combination of flourocarbons, propane, butane, isobutane, and dimethylether. The retention times of some likely propellants are listed in Table 1. Isobutane, butane, and dimethyl ether elute after the compounds R-152a and R-134a. To prevent these compounds from interfering with subsequent analyses, the oven temperature is ramped for a secondary level at 30° C/min to 245° C and held for 3.0 min.

3.2 Unless care is taken to completely evacuate the propellant collection system and sweep out any connecting lines to the bag with product before starting collection, nitrogen may be detected in the bag contents. As long as the nitrogen contamination is less than 0.1% by weight of the sample, this contamination will not affect the results of the analysis.

3.3 Components that have similar retention times to the analytes will interfere in this procedure.

4 APPARATUS AND MATERIALS

4.1 Propellant Collection System: See Figure 1. The system was built from 1/4" stainless steel and teflon tubing. The vacuum pump is of bellows diaphragm design.

4.2 Unused Tedlar Bags, 1 liter, equipped with slip valve and septum

4.3 250 ml gas dilution bulb

4.4 Gas tight syringe, 100 μl

4.5 Balance, capable of accurately weighing to 0.1 mg

4.6 Can Piercing Platform. See Figure 2

4.7 Platform Shaker, equivalent to Thermolyne M49125

4.8 Gas chromatographic system equivalent to Hewlett Packard Model 5890/Chemstation equipped with TCD and a 30 m, 0.53 mm id. Carboxen 1006 PLOT capillary column.

5 GASES AND REAGENTS

5.1 Helium, Grade 5 for gas chromatography

5.2 Quantitative Calibration Standard: A 33% v/v mixture of 1,1,1,2-tetrafluoroethane (R-134a) and 1,1-difluoroethane (R-152a) NIST traceable and carbon dioxide (CO_2).

6 PROCEDURE

6.1 Propellant Collection

6.1.1 Turn on vacuum pump, close valves and evacuate the system (see Figure 1).

6.1.2 Remove the valve actuator on the aerosol can and weigh can to the nearest 0.01 g. Invert the can into cork holding ring on the piercing apparatus, center and snug against the gasket. (Figure 2) (This works best if the aerosol can is kept refrigerated and upside down till ready for use).

6.1.3 Connect tedlar bag to output 2, evacuate bag and seal. Connect 250 ml glass dilution bulb to output 1, evacuate bulb and seal.

6.1.4 Slowly raise the hydraulic jack until the can is pierced. Note the pressure of the can.

6.1.5 Vent the can until the pressure is reduced by about 25% of maximum. Collect the propellant in the tedlar bag.

6.1.6 After the propellant is collected, close and remove the tedlar bag and vent the remainder of the propellant.

6.1.7 Weigh the evacuated 250 ml bulb to the nearest 0.1 mg. Use gloves while handling the bulb. Connect the bulb to the tedlar bag and open to fill the bulb. Close the valves and re-weigh the dilution bulb, record the weight gain and calculate the propellant density in gm/l.

6.1.8 After the flow ceases from the can, it is removed from the assembly and allowed to vent overnight. The can may be placed on a platform shaker to vent the remainder of the propellant.

6.1.9 Reweigh can to the nearest 0.01 gm and record weight loss (total gms propellant). The can may now be opened for analysis of the liquid product.

6.2 Set up the GC system to the following conditions:

Column, Carboxen 1006, 30 m x 0.53 mm id (Supelco)

Injector Temperature	280 °C
Detector Temperature	280 °C

Oven Temperature Program:

Initial:	35° C for 3.0 min.
Rate:	20° C/min to 225 °C
Hold time:	6.0 min
Second Level:	30 °C/min to 245 °C
Final time:	3.0 min
Column Flow Rate:	3 ml/min.
TCD Reference Flow:	15 ml/min
Split Vent Flow:	40 ml/min.

6.3 Inject 40 μl of Grade 5 helium as a system blank. There should be no peaks in the chromatogram. If interfering peaks appear, bake out the system until clean.

6.4 A screening analysis is done initially to determine the presence of either R-152a, R-134a or CO_2. Using the 33% mix a one-point calibration is run.

6.5 Using a 100 μl gas tight syringe with a side-hole needle (Style 5), insert the needle through the bag septum, flush the syringe with the bag contents several times, and withdraw approximately 80 μl gas. Just prior to injection, reduce the volume to 40 μl and inject into GC. This calibration will confirm the retention times of the analyte compounds.

6.6 Inject the samples using the same procedure as described in 6.5. If no R-152a or R-134a are detected the analysis is complete, indicating that all the propellant is calculated as VOC. If either R-152a or R-134a is detected, that sample will be analyzed using the pure compounds. If CO_2 is present, it is given the full exemption (generally when present it is 100%).

6.7 A four point calibration of the pure standard of R-152a or R-134a is made. This is followed by a He blank, a check of the standard at 50%v/v, and the sample(s) in question.

7 CALCULATIONS

7.1 The Total Grams Exempt VOC in the propellant is calculated as follows:

gms/L Exempt = (Molecular Weight of Exempt, gms/24.5 L) (% V/V Exempt) (assumes 25 °C)

Total Grams Exempt = (gm/L Exempt) (Grams Propellant/gm/L Propellant Density)

Alternatively, if the exempt compound comprises more than 98% of the propellent, the entire propellant mass can be declared exempt.

TABLE 1

EXEMPT COMPOUND RETENTION TIMES

COMPOUND	RETENTION TIME MIN
Nitrogen	5.87
Carbon monoxide	5.89
Methane	6.26
Trifluoromethane	7.91
Carbon dioxide	9.52
1,1,1,-Trifluoroetheane	10.23
Ethane	13.17
Pentafluoroethane	14.22
1,1,1,2-Tetrafluoroethane	14.93
1,1,-Difluoroethane	15.48

Figure 1

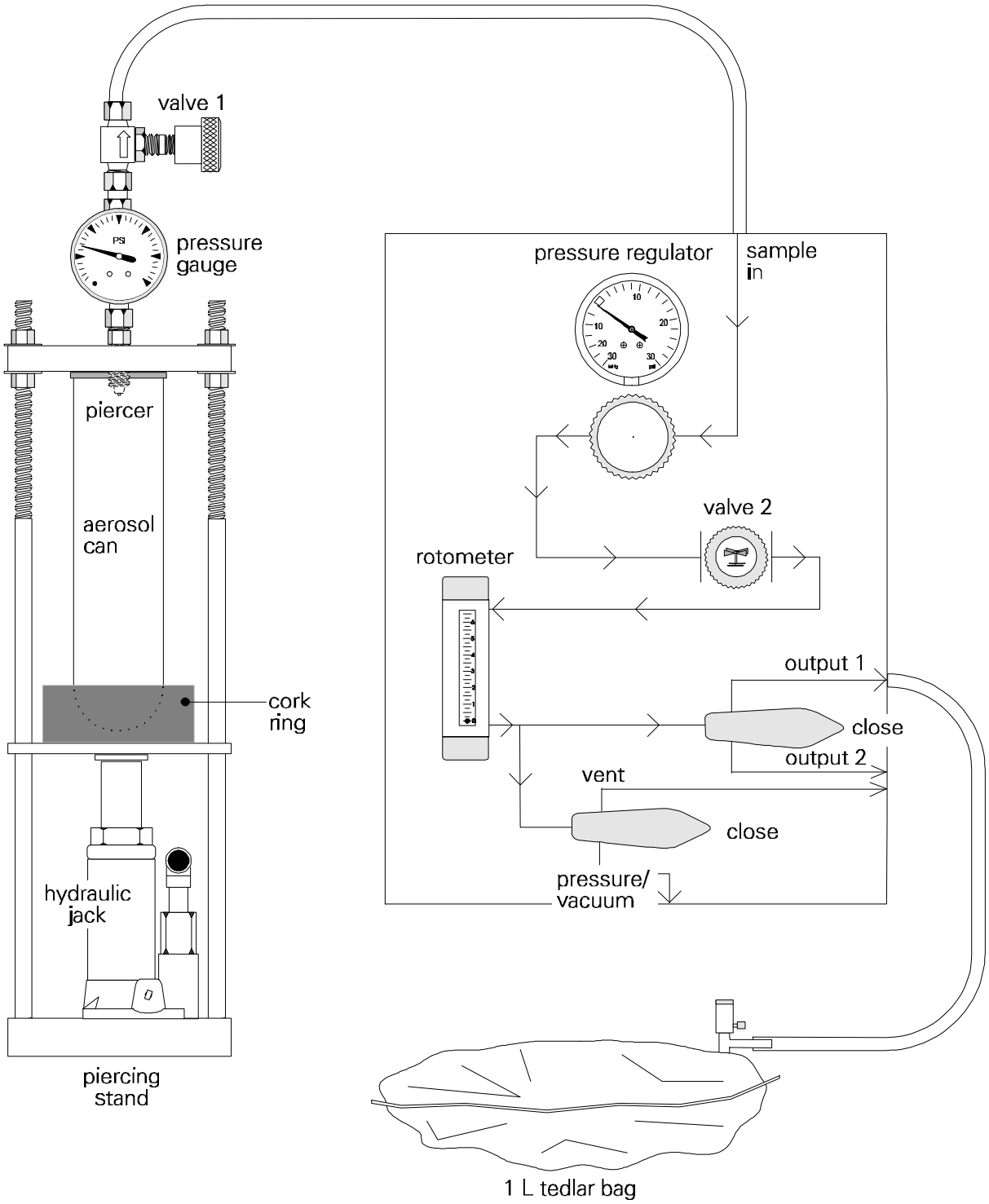
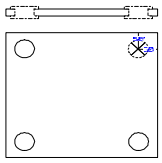
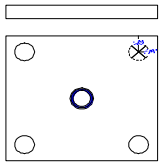

valve 1
pressure gauge
PSI
piercer
aerosol can
cork ring
hydraulic jack
piercing stand
pressure regulator
sample in
valve 2
rotometer
output 1
close
output 2
vent
close
pressure/ vacuum
1 L tedlar bag

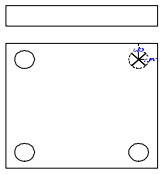
Figure 2



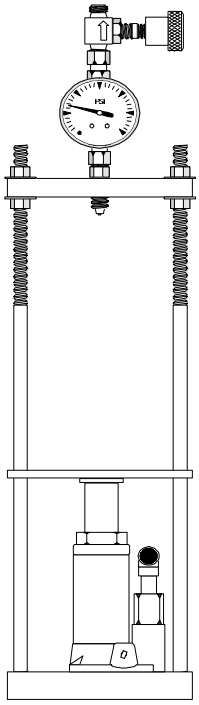
6" X 6" X 3/16" Steel Jack Plate
Center Holes 5/8" from edge
Drill 4 perimeter holes to allow for a 1/2" bushing that works with the smooth portion of the 1/2" rods
Tack weld the lift portion of the hydraulic jack to the center of the plate (weld while jack is fully extended as to not damage it)

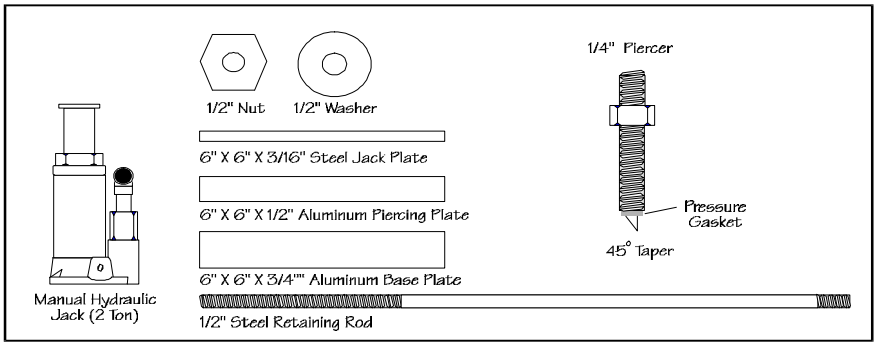


6" X 6" X 1/2" Aluminum Piercing Plate
Center holes 5/8" from edge
Drill 4 perimiter hole with 9/16" bit
Drill center holes with 7/16" bit
Tap center using 1/2 X 20 NF tap
Sample piercer is included to ensure drill bit and tap size as center hole is crucial to apparatus)



6" X 6" X 3/4" Aluminum Base Plate
Center holes 5/8" from edge
Drill 4 perimeter holes with 23/32" bit
Tap 4 perimeter holes with 1/2 X 13





Appendix A

Collection of Propellant from Aerosol Consumer Products

***System Preparation*:**

1. Turn on vacuum pump and fill dewar with ice cubes.

2. Open vacuum valve, turn zero air/vacuum valve to vacuum.

3. a. Valve #1 closed
   Valve #2 closed
   Valve #3 closed
   Valve #4 closed

   b. Connect tedlar bag to output 1.

   c. Connect density bulb to ouput 2.

   d. Rotate pressure regulator full counterclockwise (until stops).

4. Evacuate density bulb: Valve #3 turn to output 2, Valve #4 to vacuum. Wait for a few seconds until the lines are evacuated. Turn the stopcock on the density bulb a quarter turn (1/4) to evacuate the bulb. Wait a few seconds, then turn the stopcock back to close.

5. Close valve #3. Remove the density bulb and weigh and record the weight in lab book. Wear gloves whenever handling the bulb!

6. Evacuate tedlar bag: Turn Valve #3 to output 1, turn the valve on the bag one (1) turn counterclockwise. Fully evacuate the bag and close the valve on the bag (clockwise).

7. Close Valve #3 and Valve #4 (Valve #1 and #2 should already be closed.)

***Can Piercing and Propellant Collection*:**

8. The can should be centered just below the piercer, snug against the gasket (not too tight). Check that the hydraulic jack valve is closed (snug clockwise).

9. Slowly raise the jack until the can is pierced, the can pressure should be indicated on the gauge above the piercer. Raise the jack an additional 2-3 mm. Record the pressure of the can. (If the can pressure is decreasing, a good seal has not been achieved, raise the jack an additional 2-3 mm until the gauge stabilizes.)

10. Start the flow of propellant to flush the lines:

    Valve #1 open, Valve #2 open, Valve #4 vent

11. Slowly open the regulator (clockwise) while monitoring the flow meter, until there is a reading of 3-4.

12. Vent some of the propellant to purge the lines. When the pressure of the propellant is about 25 psi, start collecting the sample in the tedlar bag.

13. Rotate the pressure regulator (counterclockwise) until the flow reads “0".

14. Close Valve #4. Open Valve #3 to output 1, open the valve on the tedlar bag (one turn counterclockwise) and turn the regulator clockwise until the flow is 3-4.

15. The tedlar bag will now fill up. DO NOT OVERFILL! Close bag.

16. Rotate pressure regulator counterclockwise until flow is “0" and close Valve #3.

17. Remove the tedlar bag from the manifold.

18. Open Valve #4 to vent, increase the flow on the regulator to 3-4. Now allow the can to fully vent, until the pressure is 0. At that point the can may be removed form the manifold.

19. Denisty measurement of the propellant: The density bulb should have been evacuated and weighed. Connect the bulb to the tedlar bag, open the tedlar bag and open the stopcock on the bulb. A slight hiss will be heard as the bulb fills up. Close the bulb and close the tedlar bag. Then remove the bulb from the bag. Weigh and record the weight of the bulb.

20. Allow the can to sit overnight to continue venting.

21. Weigh the can, if the original cap was used to weigh do the same. Record the weight. This will give the weight of the propellant.

22. Open the can with the pipe cutters. Transfer the liquid portion to a 250 mL amber bottle with cap.

23. Allow the can to dry completely. (The can may be rinsed at this point with acetone to facilitate the drying.)

24. After the can is dry, reweigh the can as before. Record the weight. This will be the total weight of the liquid portion.

25. The liquid portion can now be aliquoted as described previously in the sample receipt section.

26. The bulk of the sample and the can is to be returned to the refrigerator.

Appendix B
Propellant Analysis

Aerosol consumer products must be analyzed in two phases. First the propellant must be vented from the can with minimal loss of liquid product, a representative sample collected, the density determined, and subsequent analysis by gas chromatography. The propellants primarily used are propane/butane/isobutane and dimethyl ether which are 100% voc. The more common exempt propellants are 1,1-difluoroethane (152a), 1,1,1,2-tetrafluoroethane (134a), CO_2 and N_2 and must be quantitated and subtracted from the total voc determined. The second phase is the analysis of the liquid portion which is analyzed as has been described in the method.

GC Propellant Analysis

1. Check that all gases, including the He tank for the carrier are sufficient, the tank should be changed at about 500 psi.

2. The method used initially is called SCREEN.MTH, this is used for all the aerosols to detect the presence of 152a , 134a, and CO_2 the most common exempt propellants. If present the concentration must be determined. Any of the other propellants used eg. propane/butane/isobutane are all considered VOC's and not quantitated. If 152a or 134a is present, then the sample will be run using the method specific for that compound. CO_2 if found is generally the only propellant present. If CO_2 is the only propellant it is 100 percent exempt.

3. On the GC front panel, press DET A ON. Oven temperature should be at 35. All flows have been set and should not be altered.

4. Check that the SCREEN method is in the computer. Click on Method, scroll to SCREEN, highlight and LOAD.

5. The sequence for analysis is SCREEN.SEQ. Click on Sequence, Load, SCREEN.SEQ and click LOAD.

6. Click on SEQUENCE, and highlight Edit Sequence Parameters. This is where a subdirectory of the data files will be made, corresponding to the date of analysis. In the Data File field, subdirectory type year/mon/day example: 980312A. Click on OK. You will be prompted that the subdirectory does not exist, create it? Click OK.

7. Click on Sequence, Edit Sample Log Table (This should be the rear injector.) Only a one point calibration is done for this method, to confirm the retention times. The sequence includes, a He blank and a mix of the three gases, followed by the samples.

8. There is no check sample established for this method and no QC other than the retention time check with the one-point calibration.

9. Click Sequence, Print, Sample Log Table. Print. This is the sequence table to be placed in the log book, and the first print out.

10. Click Sequence, Save. This will be saved to the SCREEN.Seq file. Replace existing file, YES. Double check the sequence.

11. Now your ready to start. Click Run Control, Run Sequence. Instrument will initialize and give box on screen showing the sample name and vial number. The system is ready to start.

12. Using a gas-tight syringe (100 μL) from a tedlar bag of He, withdraw 100 μL. Position over the rear septum. Slowly depress the plunger of the syringe until you have 40 μL. Insert the needle into the injector port and rapidly depress plunger and simultaneously press START on the gc front panel.

13. After the blank, next is the one-point calibration. The standard is an approximate 50/50% v/v of 1,1,1,2-tetrafluoroethane (134a), 1,1,1-difluoroethane (152a), and CO_2. The standard injection volume is 40 μL.

14. As in #12 above, using a gas-tight syringe withdraw 100 μL of the standard. Position over the rear port, depress the plunger to 40μL. Insert into the injection port and depress the plunger rapidly and press START on the gc front panel.

15. The samples are now ready to run. Insert the syringe into the septum of the tedlar bag, withdraw some sample and discard. Withdraw new aliquot, position over the injector port and depress the syringe until 40 μL is in the syringe, rapidly depress plunger and press start on the front panel of the GC.

16. Record and indicate any observations in the lab notebook. If no 152a , 134a or CO_2 are indicated at the given retention times, this will complete the propellant analysis. This means that all of the propellant will be counted as a VOC in the final calculations.

NOTE: If 152a or 134a is present in the SCREEN analysis, then proceed with the analysis of those samples only as follows:

17. If there is a peak that indicates either 152a or 134a, then that particular sample is to be re-analyzed using the method for 152a or 134a and a 4-point calibration using the pure compound.

18. Click on Method, select 152a (or 134a), LOAD. All of the parameters for the operations of the GC will be the same as for the SCREEN method. However now full 4-point calibration will be done to quantiate the sample.

19. Click on SEQUENCE, the sequence will be either 152a or 134a, LOAD. Click on Edit Sequence Parameters. The subdirectory in the data file field will be designated by Yr/Mon/Day and a letter to differentiate it from any earlier data file. Eg. 961015B. Click on OK and create the subdirectory.

20. Click on Sequence, Edit Sample Log Table. Fill in the number for the samples. (See example). Check that everything has been entered correctly, and print out the sample table. Be certain to SAVE in the sequence 152a or 134a.

21. The standard is calibrated on a volume percent basis. The volume injected is as follows:
    10 μL 25%
    20 μL 50%
    30 μL 75%
    40 μL 100%

22. After the calibration run, a blank is run again and a 50% check as a control. Inject 40 μL of the He blank and press start, followed by the50% check using 20 μL. (See example)

23. Now ready to run the samples. All samples are run using 40 μL injections. A check is run again at the end of the run.

SOP Revision History

1. October 16, 1996: Analysis is by an initial screening method for the presence of R-152a or R-134a. If present a 4-point calibration is made and the samples reanalyzed. The oven temperature and run time has been extended to remove propellants like isobutane and dimethyl ether from the column to minimize interference. Carbon dioxide, if present, will be 100% and given full exemption.

2. March 10, 1998. Adjusted document font to Times New Roman 12. Inserted Appendix A and B formerly a stand-alone document.